

THE SELF-DIFFUSION OF COPPER

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Abstract

This paper presents a method for obtaining rates of diffusion, particularly self-diffusion, by employing artificially produced radioactive elements. Experiments were carried out with copper. A mixture of ordinary and radioactive copper was plated onto copper blocks which were then heated at three temperatures for various lengths of time. The diffusion coefficients were calculated directly from intensity measurements of the beta rays emerging from the plated surface before and after heating. The development of the equations for the computation and the method of calculation are given. The dependence of the diffusion coefficient upon temperature was thus established. The values obtained are lower than those anticipated by Rhines and Mehl by extrapolation from binary alloy systems containing copper, but are not as low as those obtained by Rollin and by Steigman, Shockley, and Nix. A possible explanation why the values obtained by direct measurements are lower than those expected by extrapolation is suggested.

A SUITABLE technique for the study of self-diffusion of radioactive metals was first perfected in 1925 by von Hevesy and Obrucheva (4).¹ At the time of its development its use was limited to the naturally occurring radioactive substances and the initial work was carried out on lead which has the naturally occurring radioactive isotope, thorium B. The continuation of this study by von Hevesy (3), (7) and his collaborators gave one of the most complete sets of data now available, and with the series performed by Seith (7) on silver has furnished most of our fundamental conceptions concerning the theory of metallic diffusion. In view of the fact, that series of correlated experiments are the most fruitful for aiding the

¹The figures appearing in parentheses refer to the bibliography appended to this paper.

This paper is an abstract of a dissertation presented by C. L. Raynor in partial fulfillment of the requirements for the Degree of Doctor of Science at the University of Michigan, Ann Arbor, Mich.

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progress of our understanding of diffusion, Rhines and Mehl (10) carried out their investigation of the copper-aluminum, copper-beryllium, copper-cadmium, copper-silicon, copper-tin, and copper-zinc systems. A significant result of this latter investigation was the estimation of the self-diffusion coefficient of copper by the extrapolation of their data to zero concentration of solute. By this method self-diffusion coefficients could be estimated when the absence of a radioactive isotope eliminated the possibility of direct determination. The validity of the extrapolation had to await the direct determination of the self-diffusion coefficient of copper.

The availability of artificially induced radioactive metals has made possible the wider application of the von Hevesy (4) method and the continuation of self-diffusion studies. This paper describes a method for obtaining data on self-diffusion which uses artificially produced radioactive substances. The method is illustrated by the determination of the self-diffusion coefficient of copper.

PROCEDURE

Samples for study are prepared in a manner similar to that for a two-component system. The usual method of electrodeposition may be employed and it was chosen for this work. The radioactive copper was prepared by bombarding ordinary copper with deuterons in a cyclotron. The piece of copper to be made radioactive in the cyclotron is called a target and the target after bombardment is then a source of radioactive atoms.

The experimental method consisted of plating the radioactive copper onto a copper block, heating the block to allow diffusion to take place, and calculating the diffusion coefficients from intensity measurements of the beta rays emerging from the plated side of the block before and after diffusion took place.

The following characteristics of the target after removal from the cyclotron had to be considered in choosing the plating technique to be used. The source did not consist of 100 per cent radioactive copper atoms. Only a very small percentage were radioactive, and these were concentrated in that section of the target which was the focal spot for the deuteron beam and to the depth of maximum penetration of the deuterons. This was a volume approximately one-half inch in diameter by 0.005 inch deep. Its position could not be definitely located and how the radioactive atoms were distributed

in it was not determined. Using a source of this nature and plating it directly onto the sample block would result in a plate in which the distribution would be the reverse, top to bottom, of the source.

The distribution of the radioactive atoms in the plate had to be known for the purposes of calculation. This requirement was met by completely dissolving the source and converting the solution into a suitable plating bath. In solution, the distribution became uniform and when this copper was plated, using an insoluble anode, the concentration of radioactive atoms at all sections in the plate was a constant.

The desirability of having as high a concentration as possible of radioactive atoms in the plate made the following target size the most suitable to use. Because atoms at a depth greater than 0.005 inch could not be made radioactive, the targets were cut from a strip 0.005 inch in thickness. The strip was one-half inch in width which would take the entire focal spot. A sufficient length was taken for each target so that it could be easily clamped onto the target holder. The target after bombardment was cut into one-half inch by one-sixteenth inch sections and from these sections those containing the radioactive copper were selected by means of the electro-scope. The selected ones were dissolved and the plating bath prepared.

A cyanide bath (1) with a platinum anode was used. The bath was stirred and low current densities were used to insure the obtaining of smooth plates of uniform thickness. The thickness of the plates used varied from 0.00015 to 0.003 inch. The plates of less than 0.001 inch in thickness were not touched after plating. The heavier ones were smoothed on 3/0 emery paper. Before plating, the blocks were annealed in vacuum at 750 or 850 degrees Cent. (1380 or 1560 degrees Fahr.) for 24 hours to prevent any major changes in the grain size during the subsequent diffusion anneal.

The plated blocks, in an evacuated tube, were placed in a cold furnace, heated to 400 degrees Cent. (750 degrees Fahr.), and given a 1-hour soak to remove any occluded hydrogen. The agreement of intensity measurements before and after this treatment showed that no appreciable diffusion took place during this short and low temperature anneal.

For the diffusion anneal all but two of the blocks were heated in vacuum by sealing them in quartz vials. The vials were made

from quartz tubing. A length of 1 to 2 inches was used which just sufficed to enclose the blocks. In this way a temperature gradient along the vial was eliminated. The block dimensions were $\frac{1}{2}$ by $\frac{3}{8}$ by $\frac{3}{16}$ inches. No allowance was made in the time at temperature for heating and cooling of the samples. They were always placed in a furnace which was at temperature and as their heat capacity was small they rapidly reached the temperature of their surroundings. Two blocks were not heated in vacuum but in a tube through which hydrogen was continuously passed.

The plate thickness was determined by a measurement of its image at $\times 1000$ on the view plate of a metallographic camera. The average of several readings was used. The blocks treated at 650 and 750 degrees Cent. (1200 and 1380 degrees Fahr.) were measured after the diffusion anneal. This made it possible to cut and measure these blocks along two axes which crossed at right angles at the center of the block. The blocks treated at 850 degrees Cent. (1560 degrees Fahr.) had to be measured before the diffusion anneal since grain growth obliterated the plate boundary in this case. For this latter case, as the blocks had to be preserved, readings of the plate thickness were limited to one edge.

The radioactivity was measured by means of a Lauritsen (6) electroscope. Normal decay of the intensity of the source was allowed for by correcting all readings to a common base time for comparison. This was done by means of the normal decay curve for copper. Radioactive copper has a half-life period of 12.8 hours (13). This value was confirmed in the present investigation. The intensities used were the average of at least two measurements.

The copper used throughout the work was oxygen-free high conductivity copper and a spectrographic analysis showed it to be of excellent purity.

METHOD OF CALCULATION

The diffusion coefficient is defined by Fick's Law,

$$dm = DA \frac{dc}{dx} dt \quad (1)$$

From equation (1) we may derive the differential equation,

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \quad (2)$$

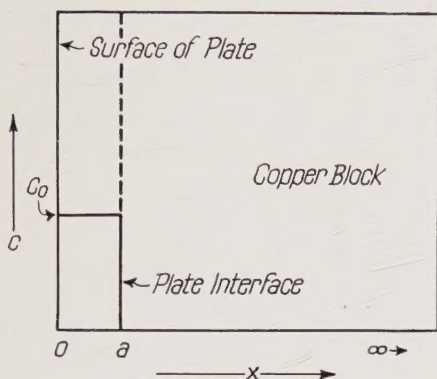


Fig. 1—Graph Showing the Initial Distribution of Solute.

For self-diffusion D may be taken out of the differential,

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (3)$$

In the solution of this equation the following limits, which apply to the experimental procedure used, must be considered:

- 1) At $t = 0$, Fig. 1,
 $c = c_0$ for $0 < x < a$
 and
 $c = 0$ for $x > a$
- 2) For $t > 0$,
 $c = 0$ at $x = \infty$

The integration of equation (3) according to these limits yields the equation of the concentration depth curve.

$$c = \frac{c_0}{\sqrt{\pi}} \int_{\frac{a+x}{2\sqrt{Dt}}}^{\frac{a-x}{2\sqrt{Dt}}} e^{-\beta^2 d\beta} \quad (4)$$

c is the concentration at the depth x after the time t .

c_0 is the initial concentration.

a is the plate thickness.

D is the diffusion coefficient.

β is an integration variable.

When the solute is radioactive we can substitute

$$\begin{aligned} i_0 &= c_0 \\ i &= c \end{aligned}$$

where i_0 and i are the intensities of the radioactive solute per unit volume.

$$i = \frac{i_0}{\sqrt{\pi}} \int_{\frac{a+x}{2\sqrt{Dt}}}^{\frac{a-x}{2\sqrt{Dt}}} e^{-\beta^2} d\beta \quad (5)$$

The intensity of beta rays emerging from a given surface of a block of copper which contains a given amount of radioactive copper is a function of the distribution of the radioactive copper in the block. This is due to the stopping power of copper for beta rays. The stopping power was determined by measuring the intensity of a source after various thicknesses of copper had been interposed between it and the electroscope. The data are shown in Fig. 2 and the equation of this curve is:

$$I = I_0 e^{-\mu x} \quad (6)$$

I is the intensity passing through the thickness x .

I_0 is the initial intensity.

μ is the absorption coefficient. Its value was found to be 786 inches⁻¹.

The intensity i' emerging from one side of the block due to an intensity i at x is given by

$$i' = A i e^{-\mu x} \quad (7)$$

A is the area of the surface.

The total intensity is the summation of all such terms as equation (7) or,

$$I = \Sigma i' = \int_0^{\infty} A i e^{-\mu x} dx \quad (8)$$

I , the total intensity emerging from the given surface can be measured.

Combining equations (5) and (8)

$$I = A \int_0^{\infty} \left[\frac{i_0}{\sqrt{\pi}} \int_{\frac{a-x}{2\sqrt{Dt}}}^{\frac{a+x}{2\sqrt{Dt}}} e^{-\beta^2 d\beta} \right] e^{-\mu x} dx \quad (9)$$

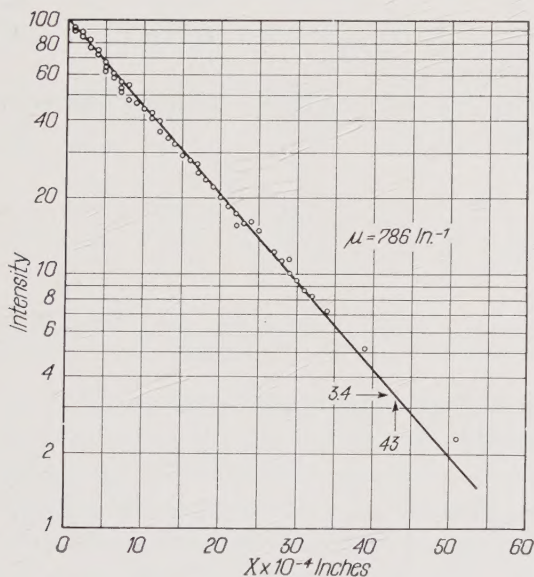


Fig. 2—The Measured Intensity (I), Expressed as Per Cent of the Initial Intensity (I_0), Passing Through Copper of Varying Thicknesses (x).

and integrating

$$\begin{aligned} \frac{I}{A} = \frac{i_0}{2\mu} e^{\mu^2 t D} \left[(e^{\mu a} - e^{-\mu a}) - \frac{2e^{\mu a}}{\sqrt{\pi}} \int_0^{\frac{a+2\mu t D}{2\sqrt{tD}}} e^{-\beta^2 d\beta} \right. \\ \left. + \frac{2e^{-\mu a}}{\sqrt{\pi}} \int_0^{\frac{-a+2\mu t D}{2\sqrt{tD}}} e^{-\beta^2 d\beta} \right] + \frac{2i_0}{\mu\sqrt{\pi}} \int_0^{\frac{a}{2\sqrt{tD}}} e^{-\beta^2 d\beta} \quad (10) \end{aligned}$$

we have the equation for calculating D from intensity measurements of the beta rays emerging from the plated side of the block. I can be measured at any time (t) by means of the Lauritsen electro-scope.

$$\frac{2}{\sqrt{\pi}} \int_0^y e^{-\beta^2} d\beta \quad \text{is the probability integral.}$$

The values of this integral when the limit (y) is known are given in mathematical tables (8).

i_0 can be calculated by substituting the initial conditions in equation (8) and solving:

$$I_1 = A i_0 \int_0^a e^{-\mu x} dx$$

$$i_0 = \frac{I_1 \mu}{A (1 - e^{-\mu a})} \quad (11)$$

I_1 is the initial intensity from the plated surface.

Combining (10) and (11)

$$I = \frac{I_1 e^{\mu^2 t D}}{2 (1 - e^{-\mu a})} \left[(e^{\mu a} - e^{-\mu a}) - \frac{2 e^{\mu a}}{\sqrt{\pi}} \int_0^{\frac{a + 2 \mu t D}{2 \sqrt{t D}}} e^{-\beta^2} d\beta \right. \\ \left. + \frac{2 e^{-\mu a}}{\sqrt{\pi}} \int_0^{\frac{-a + 2 \mu t D}{2 \sqrt{t D}}} e^{-\beta^2} d\beta \right] + \frac{2 I_1}{\sqrt{\pi} (1 - e^{-\mu a})} \int_0^{\frac{a}{2 \sqrt{t D}}} e^{-\beta^2} d\beta \quad (12)$$

The diffusion coefficient D may be calculated from this equation, using the data of Table I, by the method of trial and error.

RESULTS AND DISCUSSION

The self-diffusion coefficient for copper was determined at three temperatures and the effect of temperature on the rate of diffusion

Table I
Data Used and the Diffusion Coefficients Determined

Sample No.	Block Annealing Temp. Degrees Cent.	Diffusion Temperature Degrees Cent.	Plate Thickness Inch	Initial Intensity I_1 Sec. ⁻¹	Final Intensity I Sec. ⁻¹	Time at Temperature Hours	Diffusion Coefficient Cm. ² /Sec.
10	850	650	0.00023	$1.83 \cdot 10^{-2}$	$1.53 \cdot 10^{-2}$	85.6	$2.03 \cdot 10^{-12}$
11	850	650	0.00015	$1.26 \cdot 10^{-2}$	$9.75 \cdot 10^{-3}$	85.6	$3.17 \cdot 10^{-12}$
17	850	650	0.00015	$1.18 \cdot 10^{-2}$	$8.90 \cdot 10^{-3}$	69.9	$4.57 \cdot 10^{-12}$
22	850	650	0.00058	$8.85 \cdot 10^{-2}$	$7.44 \cdot 10^{-2}$	93.9	$3.68 \cdot 10^{-12}$
23	850	650	0.00050	$8.76 \cdot 10^{-2}$	$7.57 \cdot 10^{-2}$	93.9	$2.53 \cdot 10^{-12}$
Av. = $3.20 \cdot 10^{-12}$							
1	750	750	0.0014	$9.16 \cdot 10^{-2}$	$5.94 \cdot 10^{-2}$	96.2	$3.35 \cdot 10^{-11}$
4	750	750	0.0028	$6.41 \cdot 10^{-2}$	$5.97 \cdot 10^{-2}$	103.0	$1.34 \cdot 10^{-11}$
6	750	750	0.0016	$6.06 \cdot 10^{-2}$	$4.40 \cdot 10^{-2}$	106.0	$2.29 \cdot 10^{-11}$
18*	850	750	0.0015	$1.84 \cdot 10^{-2}$	$1.31 \cdot 10^{-2}$	77.0	$2.96 \cdot 10^{-11}$
19*	850	750	0.0014	$1.94 \cdot 10^{-2}$	$1.43 \cdot 10^{-2}$	77.0	$2.53 \cdot 10^{-11}$
Av. = $2.49 \cdot 10^{-11}$							
20a	850	850	0.0017	$3.54 \cdot 10^{-2}$	$2.24 \cdot 10^{-2}$	24.0	$2.79 \cdot 10^{-10}$
20b**	...	...		$3.54 \cdot 10^{-2}$	$1.81 \cdot 10^{-2}$	46.0	$2.35 \cdot 10^{-10}$
21a	850	850	0.0020	$3.66 \cdot 10^{-2}$	$2.42 \cdot 10^{-2}$	24.0	$2.90 \cdot 10^{-10}$
21b	...	...		$3.66 \cdot 10^{-2}$	$1.98 \cdot 10^{-2}$	46.0	$2.44 \cdot 10^{-10}$
Av. = $2.62 \cdot 10^{-10}$							

*Annealed in hydrogen.

**The same sample as 20a but put back in the furnace for an additional 22 hours.

was obtained, Fig. 3. The experimental variation of the data is shown. The validity of the data, however, can best be shown by a consideration of the individual measurements although the accuracy of D is subject to the interrelation of the variables with each other.

The Absorption Coefficient of Copper for Beta Rays—The magnitude of D is not sensitive to even rather large changes μ . The value of μ is given by Steigman, Shockley and Nix (12) as 700 inches⁻¹, but when this value is used instead of that determined in this work no appreciable change in D is noted.

Intensity Measurements—The average deviation of the intensity measurements, from the mean of all readings for that intensity determination, was 1.5 per cent. A maximum error of this amount in both intensity measurements or a 3 per cent error in the ratio would show an average error of 14 per cent in D . It is thought that the error from this source was considerably less.

The Plate Thickness—Great care had to be taken in the plating operation. This is necessary when the entire width of a plate and thus the outside edge is used. Every precaution was taken to have as smooth a surface as possible. Some individual measurements varied as much as 50 per cent from the mean. However, the aver-

age was much better as shown by the following. All of the samples except those treated at 850 degrees Cent. (1560 degrees Fahr.) were repolished at least once and the average variation of the reading for each polish from the mean was only 8 per cent. Hence, the error from this source was less than 10 per cent.

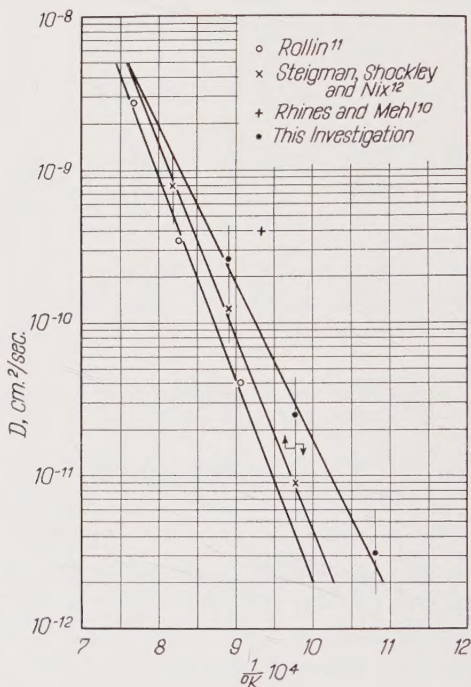


Fig. 3—The Self-Diffusion Coefficient of Copper Versus Temperature.

Temperature—Small variations in temperature are not distinguishable on the scale used for the plot.

Time—There was no uncertainty in this measurement.

It is to be noted that the depth-concentration curve was not used for the calculation and thereby the uncertainties associated with its use were avoided.

The determination of the self-diffusion coefficient of copper renders more complete Rhines and Mehl's (10) series of measurements on the copper-aluminum, copper-beryllium, copper-cadmium, copper-silicon, copper-tin and copper-zinc systems. Their extrapo-

lated value of 4.10^{-10} centimeter per second squared at 800 degrees Cent. (1470 degrees Fahr.) seems to be too high. This is shown in Fig. 3. This is undoubtedly due to the inaccuracy of their data at the concentration limits, as mentioned by them, and the necessity of extrapolation from the regions of rather high concentration. At very low concentrations it is likely that the diffusion coefficient does decrease and approach the self-diffusion coefficient of copper. Or, starting with pure copper, for solute additions of very much less than 1 atomic per cent the diffusion coefficient increases rapidly. The rate of increase then falls off and only increases slightly until the limit of solubility is reached. Close to the limit of solid solubility the rate of increase of the diffusion coefficient is again rapid.

This conception of the shape of the curve at low concentrations can be understood from the following considerations. Whatever the crystal form of the solvent is, the introduction of a foreign, solute atom into this lattice disarranges it. This condition allows for the more rapid penetration of additional solute atoms through the solvent lattice. However, for solute atoms to aid each other in this way, there must be enough present so that the effect of one is noticeable to another. Or, the solute atoms must be close enough together so that the disorder caused by one is not smoothed out in the interval between it and another solute atom. The effect at low concentrations is therefore that a rapid increase in the rate of diffusion results from small increases in the amount of solute added. The slope of the curve falls off as soon as there is enough solute present to make the disorder of the solvent lattice practically continuous. The lower values of concentration for which Rhines and Mehl (10) determined the coefficients were on the plateau portion of the curve. The extrapolation, therefore, gave an incorrectly high value of the self-diffusion coefficient.

Also shown in Fig. 3 are the results of two other investigations (11, 12) on copper which were published after the inception of this work. The methods were sufficiently different and this work had advanced so far it was decided that it was worthy of completion.

A modification of the Dushman-Langmuir equation (2),

$$D = A e^{-\frac{Q}{RT}},$$

was used to represent the data. The Q values, Table II, show that the slope of the curve representing the data obtained in this investi-

gation is in closer agreement with the expected value as given by Rhines and Mehl (10) and by Kanter (5, 9). The extrapolated value of Rhines and Mehl (10), however, would be expected to be low due to the same considerations as discussed for the diffusion coefficient. As the diffusion coefficient decreases and the total amount of diffusion is less, slight variations in the handling and measurement of the samples have greater weight. Thus a greater variation in the data is to be expected at the lower temperatures.

Table II
Summary of the Q Values for the Dushman-Langmuir Equation,

$$D = A e^{-\frac{Q}{RT}}$$

Rhines and Mehl (10)	44,000 cal./mol.
Kanter*	39,000 " "
Rollin (11)	61,400 " "
Steigman, Shockley and Nix (12)	57,200 " "
This investigation	46,800 " "

*Private communication to Rhines and Mehl (10). The method is given in reference 5.

Many times the question of interference to diffusion by the interface between the electrodeposited layer and the body of the sample has been mentioned. The agreement between the data of Rollin (11), and Steigman, Shockley and Nix (12), and this work show that electrodeposition is a satisfactory method for preparing diffusion samples. Rollin (11) used a direct method for preparing his samples which eliminated such an interface.

In Table I it is noted that two samples were run in hydrogen. No effect due to this was noted in the coefficients calculated from these samples. Also, no difference was observed by a change in the block anneal from 750 to 850 degrees Cent. (1380 to 1560 degrees Fahr.), although the grain size was somewhat larger at 850 degrees Cent. (1560 degrees Fahr.). During the 650 and 750 degrees Cent. (1200 and 1380 degrees Fahr.) diffusion anneals, the grain size remained practically constant. However, during diffusion at 850 degrees Cent. (1560 degrees Fahr.) there was continuous grain growth. This was why the plate thickness on these blocks had to be measured before the anneal as the grains grew across the boundary and obliterated it. This also did not produce a noticeable effect in the results of this test.

SUMMARY

A method for obtaining data on diffusion which uses artificially produced radioactive substances has been presented.

The self-diffusion coefficient for copper was determined at three temperatures and the dependence upon temperature obtained. The rate of diffusion is lower than was expected from the value given by Rhines and Mehl (10).

The method of calculation is presented and it is shown that assumptions which are inherent in other methods may be eliminated.

ACKNOWLEDGMENT

The helpful assistance of Professor J. M. Cork and his collaborators of the Physics Department of the University of Michigan is gratefully acknowledged.

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